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DEVELOPMENT OF RADIATION HARD SCINTILLATORS

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Abstract

We have demonstrated that the radiation stability of scintillators made from styrene polymer is very much improved by compounding with pentaphenyltrimethyltrisiloxane (DC 705 vacuum pump oil). The resulting scintillators are softer than desired, so we decided to make the scintillators directly from monomer where the base resin could be easily crosslinked to improve the mechanical properties. We can now demonstrate that scintillators made directly from the monomer, using both styrene and 4-methyl styrene, are also much more radiation resistant when modified with DC705 oil. In fact, they retain from 92% to 95% of their original light output after gamma irradiation to 10 Mrads in nitrogen with air annealing. When these scintillators made directly from monomer are compared with scintillators of the same composition made from polymer the latter have much higher light outputs. They commonly reach 83% while those made from monomer give only 50% to 60 % relative to the reference, BC408. When oil modified scintillators using both p-terphenyl and tetraphenylbutadiene are compared with identical scintillators except that they use 3 hydroxy-flavone as the only luminophore the radiation stability is the same. However the 3HF system gives only 30% as much light as BC408 instead of 83% when both are measured with a green extended Phillips XP2081B phototube.

* Operated by the Universities Research Association, Inc., for the U.S. Department of Energy.

Introduction

J. Harmon et al. from the University of Florida showed that poly(hexylmethacrylate) is much more radiation stable than polymethylmethacrylate, and attributed this to the lowering of the glass transition temperature and correlated that with permeability.^{1,2,3,4}

F. Markley et al. from Fermi National Accelerator Laboratory showed that adding pentaphenyltrimethyltrisiloxane to polystyrene based scintillators made a large improvement in their radiation stability.⁵ They attributed this to an increase in the diffusion rate, and therefore of the recombination rate, of free radicals produced by the radiation. The oil additive also lowers the glass transition temperature. It is commercially easier to add an existing oil than to synthesize a new polymer, so we have concentrated our efforts in this direction. The most important mechanical requirements of a scintillator are that it must not craze or cold flow. The oil additive might actually improve the craze resistance of the scintillator, but it will also certainly increase the cold flow. It seemed desirable therefore to make scintillator from monomer where it is easy to crosslink the monomer and thus reduce any cold flow problems. The present work demonstrates that such scintillators are indeed radiation stable, but has not yet proven the desired improvement in cold flow resistance. Crosslinked scintillators of the desired properties evidently require very careful control of the reaction conditions and perhaps selection of the difunctional crosslinking agent and its concentration. Since we have found that the scintillators from monomer have a considerably smaller light output than those from polymer, we now feel it to be worthwhile to pursue both scintillators from polymers and from crosslinked monomers. The desired level of cold flow stability in the case of scintillators from polymers may be achieved by slight reductions in the concentration of the oil or by finding some different oil. In fact the present formulation using 70 parts of Dow polystyrene, 30 parts of DC705 vacuum pump oil, 2 parts of p-terphenyl and .2 parts of tetraphenylbutadiene (by weight) may be adequate, so we are undertaking scale-up studies with this formulation. A group of tiles 11x 11x.3cm have been fabricated by casting, machined with key-hole shaped grooves and irradiated with readout shifter fibers. These tiles with fibers are presently annealing and in process data will be presented at this conference. The scintillators from polymer are being made at Fermi, and those from monomer are being made at the University of Florida. The irradiations and annealing measurements are being made at the University of Michigan. The Polycal Group⁶ are investigating different diffusion enhancing modifiers, and are making scintillators both from monomer and from polymer. Their data confirms the U.S. data and they have the capability of producing commercial quantities of scintillator from any new formulations.

Polymerizing Samples

Samples were polymerized in sealed glass vials at 80 - 90° centigrade for 12 to 14 hours.

Irradiation

Samples were soaked in nitrogen and radiated in nitrogen at 1Mrad per hour then annealed in air.

Measurements

At Michigan light outputs were measured by anode current from a Phillips XP2081B photomultiplier tube.

At Fermi light outputs were measured by pulse height from a Hamamatsu R2154 photomultiplier tube.

Results

Eight samples were made from monomer at the University of Florida. Four of these were made from styrene and four from 4-methyl-styrene. In each group of four, two were made with DC705 oil and two without. Also two were made with divinylbenzene as a crosslinking agent and two without. The basic formula was either 100 parts by weight of monomer or 70 parts of monomer and 30 parts of DC705. All samples had 2 parts of p-terphenyl and .2 parts of tetraphenylbutadiene and .1 parts of L-231 polymerization catalyst. When the DVB crosslinking agent was used, it was used at .2 parts. All of the samples were 1 cm thick by 2.2 cm in diameter and they were soaked in nitrogen, irradiated in nitrogen, and annealed in air.

Figure 1 shows the annealing curves of the styrene samples which were not cross-linked. The superiority of the sample containing the DC705 is immediately evident. Figure 2 shows the annealing behavior of the styrene samples that were crosslinked with DVB. Again the superiority of the sample with the DC705 is obvious. Figures 3 and 4 show the similar results for the samples using 4-methyl-styrene as the base plastic. In both the crosslinked and not crosslinked cases the samples with the DC705 are much superior. The major difference seen in the 4-methyl-styrene samples compared to the styrene samples is their significantly higher light output, 80% compared to 60%. It should be noted that with all four samples with DC705, there is little or no annealing behavior and the initial light output is somewhat higher.

Figure 5 shows the annealing curves of four samples made from styrene monomer in the Ukraine and irradiated and tested in the U.S. Two samples contain diffusion enhancers different from DC705. They are labeled A and B. Only the A modifier is seen to be effective. The ST24 is a metallo-organic stabilizer. Once again, we see that the sample with the effective diffusion enhancer is superior to the other samples, but in this case the three inferior samples are still annealing, so that we cannot be sure about the comparative amount of permanent damage.

Figure 6 shows the annealing curves of the two DC705 modified samples from monomer with the data for several identical samples except that they were made from polymer. The light output of the samples made from polymer is

SYTRENE SCINTILATOR FROM MONOMER NOT CROSSLINKED

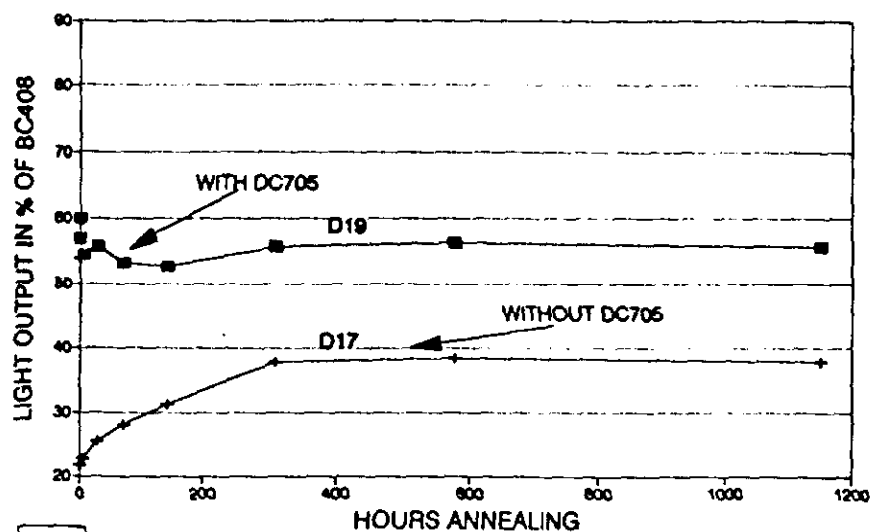


FIG. 1

STYRENE SCINTILATOR FROM MONOMER CROSSLINKED

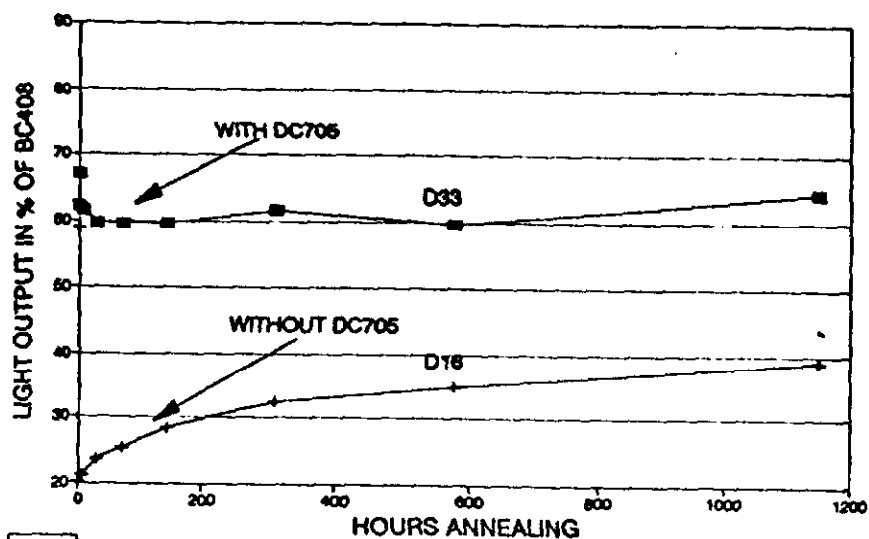


FIG. 2

VINYLTOLUENE SCINTILATOR FROM MONOMER NOT CROSSLINKED

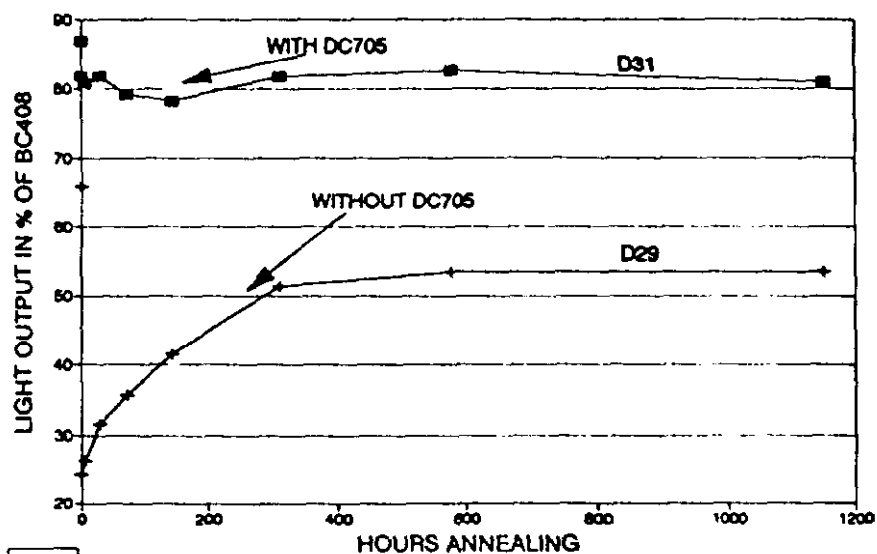


FIG. 3

VINYLTOLUENE SCINTILATOR FROM MONOMER CROSSLINKED

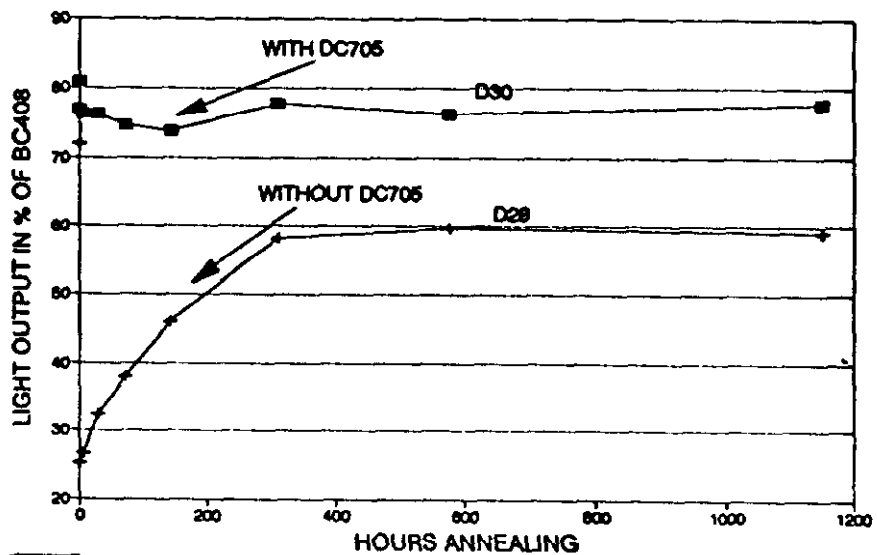


FIG. 4

ALL SAMPLES
STYRENE
+ 2 % PT
+ 02 % POPOP

M621	20 % A	01 % 6724
M623	20 % B	01 % 6724
M625		01 % 6724
M585		

621
625
585-2
623

LIGHT OUTPUT IN % OF BC408

HOURS ANNEALING

FIG. 6

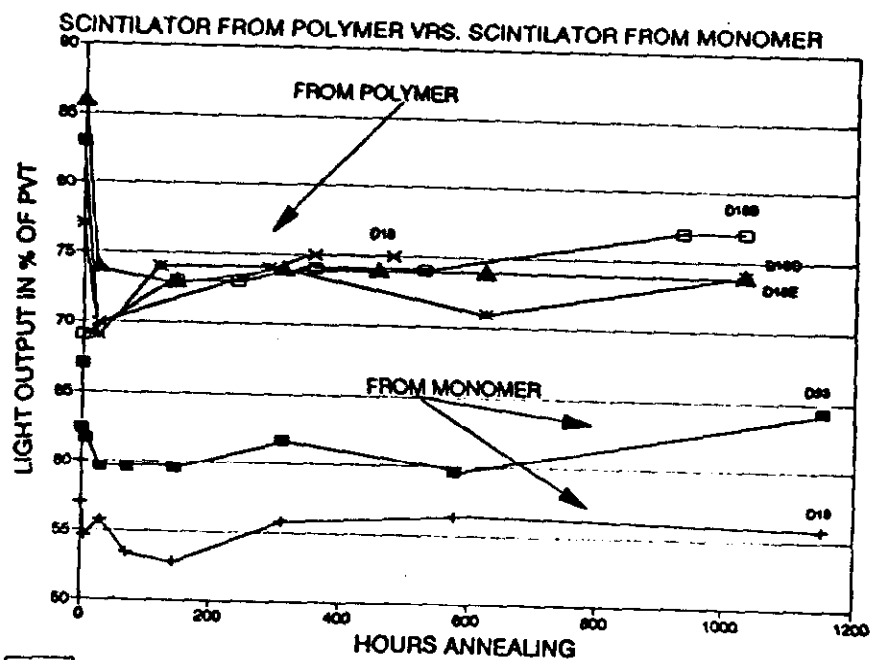


FIG. 6

significantly higher. This may be due to differences in the molecular weight and molecular weight distribution. Our Ukrainian collaborators report the same difference between scintillators from monomer and those from polymer.

The rad hardness (percent of light retained after irradiation) of the two samples from monomer is slightly, but not significantly, greater than that of the four samples from polymer. This is true both immediately after irradiation and after annealing. Samples made in the Ukraine from polymer and monomer have shown much higher rad hardness for the samples from polymer when measured immediately after irradiation (Senchishin et al. this conference). However the specific formulations used were very different in the two cases.

Conclusions

The addition of pentaphenyltrimethyltrisiloxane improves the radiation stability of scintillators made from styrene polymer, styrene monomer, and 4-methyl-styrene monomer. The light output of scintillators made from polymer is greater than the light output of similar scintillators made from monomer. The light output of 4-methyl-styrene scintillators is greater than that of styrene scintillators. Crosslinking does not effect the light output or radiation stability of scintillators made from monomer.

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5. F. Markley, et al., *Development of Radiation Hard Scintillators*, Radiation Physics and Chemistry, V41, no. 1/2, (Jan/Feb 1993).
6. The Polycal Group is a collaboration between JINR at Dubna, Russia; and Kharkov State University, Kharkov, Ukraine; and the Institute for Single Crystals, Kharkov, Ukraine. It is headed by Prof. Zalubovsky of Kharkov State University, Prof. Seminozhhenko of the Institute for Single Crystals, and Prof. Budagov of JINR. Its scientific representative is Dr. Senchishin.
7. Dr. Pla has made two scintillators from styrene monomer with 3HF, one with DC705 and one without, and found no difference in their radiation hardness in the fully annealed condition.